

HYGROSCOPICITY OF MINERAL SOIL PARTICLES  
AS AFFECTED BY SIZE OF PARTICLE AND ADSORBED CATIONS

by

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## INTRODUCTION

Soil and water relationships have always been important factors influencing civilization; yet there are many facts concerning these relationships which are not known to-day. Although the clay fraction of the soil is the most active it is the portion about which the least accurate knowledge has been obtained, principally because it is the most difficult portion to study. Any discussion on soil and water relationships involves the use of terms more or less limited to this field.

The temperature at which hygroscopic water is driven from the soil and combined water is not depends upon the type of soil (Baver and Horner, 1933), however, the generally accepted temperature is  $110^{\circ}$  C. The lower the water content the greater the force with which the water is held, giving a curvilinear relationship between the two. Thus the selection of any point on the curve for fractionation is arbitrary and different methods of procedure give various results. The hygroscopic coefficient will be considered as the percentage of moisture adsorbed over 3.3 percent sulfuric acid within five days at  $25^{\circ}$  C. in an evacuated humidifier. Hygroscopic water includes all non-combined water up to and including the hygroscopic coefficient. The process

by which soil particles remove water molecules from the surrounding atmosphere and retain them in a surface layer is called adsorption. Moisture equivalent is the percentage of water retained by a soil after being subjected to a centrifugal force of 1000 times gravity for an arbitrary time of 30 to 40 minutes. Only a general relationship exists between the hygroscopic coefficient and moisture equivalent. The most common conversion factor is 0.37 thus making the hygroscopic coefficient equal to the moisture equivalent times 0.37. The classification of soil particles as established by the United States Department of Agriculture is followed and all clay is considered to be colloidal. The determinations and definitions usually applied to soil are considered to hold for soil separates. Knowledge of the relationship of hygroscopicity to surface area is incomplete; therefore, this study was undertaken to establish facts concerning the effects of surface area on adsorption of water vapor by mineral soil particles.

#### REVIEW OF THE LITERATURE

In general the percentage of water adsorbed over both 30 percent and 3.3 percent sulfuric acid varies with the soil type but greater differences are brought out by using the drier atmosphere of the 30 percent solution.

Loughridge (1894) observed the clay fraction adsorbed more hygroscopic moisture than the entire soil and noted that consistently the finer the soil "grains" the greater the hygroscopic coefficient. Adobe clay adsorbed as much as 22.25 percent moisture while the sands adsorbed less than one percent. However, he also observed that increases in moisture held were not proportional to the amount of combined surface area presented by the soil particles, but varied directly as humus content, hydrated silicates and aluminum, and ferric hydrate.

The adsorption of water from the atmosphere over 10 percent sulfuric acid by artificially prepared soil colloids varied greatly depending upon the type of material used, according to Beaumont (1919). Ferric oxide particles adsorbed  $9.5 \pm 0.04$  percent water while silica adsorbed  $58.1 \pm 0.25$  percent. These data substantiate the theory that hygroscopicity varies with the composition of the soil as well as the amount of surface exposed by the soil particles. Beaumont (1919) also observed that soils left in a humidifier over 10 percent sulfuric acid would not come to complete equilibrium within three months. For general use, however, he recommended exposure for five days. Duplicates did not check well so five replicates were used. Soil which was air dried and remoistened adsorbed less moisture than

that kept continually moist, the difference being greatest in soils of high organic content. He considered the drying of the soil affected indirectly the reversibility of its colloidal condition through biological and chemical action.

The forces which cause nitrogen adsorption by particles are possibly similar to those which cause water adsorption. Ogg and Hendrick (1920) measured the amount of nitrogen taken from ammonium sulfate by granite particles ground to various sizes to simulate soil separates. They found that the most finely divided granite had the greatest affinity for nitrogen, but the increase was not proportional to the increase in surface area. Surface area was calculated by assuming the particles to be spherical with a specific gravity of 2.65. The formula used was:  $\text{Surface (cm}^2\text{)} = \frac{\text{Wt. sample} \times 4\pi r^2}{\text{specific gravity} \times \frac{3}{4}\pi r^3}$  which reduces to:  $(\text{cm}^2) =$

$\frac{\text{Wt. sample} \times 3}{\text{specific gravity} \times r \text{ (cm)}}$ . Keen and Raczkowski (1921)

found volume weight and specific gravity to vary inversely as the percentage of clay in the sample while pore space, volume expansion, and amount of water taken up per unit weight of soil varied directly with this percentage. The average adsorption of water by ultra clay (.1 micron or below) as determined by Robinson (1922) was .298 gm. per gram of colloid for various Missouri soils, however, the

variation was from .240 to .348 gm. He suggested that the percentage of colloidal material in a soil could be determined by dividing .298 into the amount of water adsorbed by the entire soil under the conditions of his experiment. He exposed 2 gm. of soil to the atmosphere over two percent sulfuric acid at 30° C. for five days with the container evacuated to 50 mm. or less of mercury. Anderson, et al. (1922) divided a Huntington loam soil into a coarse fraction a fine fraction, and colloidal material. They measured adsorption of malachite green, ammonia, and water and found that adsorption increased as the size of particle decreased. Adsorption of these same materials was measured by Gile, Middleton, et al. (1924) on the whole soil and on the colloidal extract of each of 32 different soils. They presented a method of estimating the percentage of colloidal material in a soil based on the adsorption per gram of soil and per gram of soil colloid. Sources of error involved in this process are, (1) getting a representative colloidal sample, and (2) change in adsorptive capacity upon extraction.

A soil was divided into 12 fractions by DeYoung (1925) who found a direct relationship between specific surface and the moisture equivalent when crystalline particles free from colloidal material were studied, and indicated that the use of a super-centrifuge which exerted a force of 30,000 times



gravity for making the two finest fractions may have disrupted the continuity of the relationship. He ran moisture equivalent on moist, oven dried, ignited, and hydrogen peroxide treated separates. Oven drying lowered the moisture equivalent on all separates but lowered it most on the finer and least on the coarser separates. The percentage lowering ranged from 61.3 to .33. Ignited samples down to the .005 - .002 millimeter separate had about the same or slightly higher moisture equivalent than the moist or oven dried ones. Below this point the ignited samples ran lower than the moist samples in all cases and lower than the oven dried in all cases but one. Moisture equivalents of the hydrogen peroxide treated separates ran close to those of the moist samples, exceeding them three times out of nine. A direct relationship existed between specific surface and moisture equivalent of each of the separates between 0.5 mm. and 0.005 mm. in diameter. Below 0.005 mm. DeYoung thought colloidal material remained a part of the separates and could be distinguished by the yellow color as compared to the white color of all larger separates.

Bradfield (1925) analyzed several soils and their colloidal content from various sections of Missouri and found the  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , volatile matter, and hygroscopic moisture remained constant in the 11 soil colloids (below



.1 micron). The colloidal matter contained a lower percentage of  $\text{SiO}_2$ , but a higher percentage of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  than the entire soil. Robinson and Holmes (1924) compared the composition of the colloidal material to that of the entire soil. The soil colloids were higher in alumina, iron, water of combination, organic matter, magnesia, phosphorus, and sulfur; but lower in silica than the entire soil. A direct relationship between the  $\text{SiO}_2 - \text{R}_2\text{O}_3$  ratio and adsorption of water vapor by soil colloids was found by Anderson and Mattson (1926). Anderson and Byers (1931) found a general increase in the amount of water adsorbed over 30 percent sulfuric acid with an increase in the  $\text{SiO}_2 - \text{R}_2\text{O}_3$  ratio, however, the relationship was not so marked over 3.3 percent sulfuric acid. The thickness of the hygroscopic water film does not exceed four or five millimicrons as determined by Mattson (1932). He believes that the quantity of water held by molecular attraction by the soil is a function of surface and is independent of the nature and quantity of exchangeable cations; however, molecular attraction is not the only method by which water is held. He lists the following factors affecting the amount of water soil colloids will imbibe.

1. Their composition, or more directly upon exchange capacity
2. Nature of exchangeable cations
3. Charge of the particles
4. Position of iso-electric point, if amphoteric or
5. Their ultimate pH, i.e. the strength of their acid group
6. The concentration of free electrolytes and the valence of the ions, both according to Donnan equilibrium

Hygroscopicity of soil colloids over 30 percent and 3.3 percent sulfuric acid was determined by Bayer and Horner (1933). They concluded "hygroscopicity over the 3.3 percent sulfuric acid appeared to be some function of specific surface." however, the hygroscopic water increased and the combined water decreased with the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio. Their results also showed that removal of organic matter had little effect on the amount of water taken up by the colloid. Winterkorn and Bayer (1934) ground particles into the following size groups: below 0.053 mm. in diameter, between 0.053 and 0.10 mm., and between 0.10 and 0.25 mm. in diameter. They observed that water adsorption and swelling increased with the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio. Particles over 0.10 mm. in diameter showed the greatest amount of swelling probably due to the dispersion effects of the water. These authors, however, working with the adsorption of H-clay at various temperatures found that by increasing the temperature from 30° to 40° C. the percentage of water taken up

was decreased 50 percent when other factors, including vapor pressure as controlled by the concentration of sulfuric acid, were kept constant. Swelling was not manifest in soil particles greater than one micron in diameter under the conditions studied by Whitt and Baver (1937). They also noted a wide break in the base exchange capacity occurred at about the same point. The fraction, 1.0 to 0.05 micron, was almost entirely absent from the soil, which possibly indicates a change in mineral composition at this point. Similar observations were made by Bray (1937). Wilcox (1939) working with irrigated soils showed there was a direct relationship between the moisture holding capacity and the percentage of silt and clay, the coefficient of correlation being .930. When moisture holding capacity was correlated with percentage colloid the correlation coefficient was .886. The corresponding value expressing the relationship between moisture holding capacity and percentage sand was -.930. This in a general way indicates that coarser particles hold less water physically than finer particles.

Baver (1928) determined hygroscopicity over two percent and 30 percent sulfuric acid, moisture equivalent, heat of wetting, and several other properties of colloids saturated with various cations and of the corresponding natural soils. Calcium, hydrogen, magnesium and manganese ions caused no

significant effect on moisture equivalent, hygroscopicity, or heat of wetting. Potassium ions caused no significant change in moisture equivalent, but decreased hygroscopicity as determined over both two percent and 30 percent sulfuric acid. Sodium ions increased the moisture equivalent, decreased hygroscopicity over 30 percent sulfuric acid and decreased the heat of wetting. He concluded that sodium and potassium ions caused a decided change in the amount or the nature of the colloid in the soil or both. Some of the difference in moisture adsorbing ability of soil saturated with different ions was attributed to the degree of hydration of the ions, by Thomas (1928). From relatively dry atmospheres the least water was adsorbed by the potassium treated material and the most by calcium treated, but from humid atmospheres the sodium saturated soil tended to have the highest water adsorbing power. Hygroscopicity with respect to the various ions at low humidity was  $\text{Ca} > \text{H} > \text{Na} > \text{K}$  and at high humidity was  $\text{Na} > \text{Ca} > \text{H} > \text{K}$ . He also noted a relationship of the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio to the properties of the soil colloid until the ratio reached 2.8. Above this point the relationship seemed to disappear. Water adsorption of soil colloids over 30 percent sulfuric acid for several cations was determined by Anderson (1929) with the ranking as follows:  $\text{Ca} > \text{Mg} > \text{K} > \text{Na} > \text{H} > \text{Methylene blue}$

cation. Mattson (1932) ascribed the greater amount of water imbibed by the sodium saturated colloid as compared to the calcium saturated colloid to the greater degree of dissociation of the sodium causing a greater osmotic pressure. According to Bayer and Horner (1933) the order of hygroscopicity over 30 percent sulfuric acid for seven cations was  $H > Ca > Li \bar{=} Mg > Na \bar{=} Ba > K$ . They pointed out this sequence is difficult to explain on the basis of hydration only, since calcium and magnesium saturated colloids contained more water than lithium and sodium saturated colloids respectively. They decided that the size and number of ions as well as the ionic hydration had an influence. The more volume taken by the ions the less there was left for the adsorbed water molecules. By using the ionic radii they calculated the ionic volumes and the relative ionic volumes of the exchangeable cations in the colloid when the relative volume of the hydrogen ion is used as unity. The theoretical hydration of clays according to the effective volumes would then be  $H > Mg > Ca > Li > Ba \bar{=} Na > K$ . They also reported that the amount of water adsorbed varied inversely with the percentage of  $Al_2O_3 + Fe_2O_3$  and directly with the percentage of  $SiO_2$ . Hygroscopicity over 3.3 percent sulfuric acid, however, was not affected by the nature of the colloid but appeared to be some function of specific surface. Removal

of the organic matter had little effect on the hygroscopicity. Combined water varied inversely with the  $\text{SiO}_2\text{-R}_2\text{O}_3$  ratio. Russell (1935) after working with adsorption of liquids by clays made the following statement: "Clays adsorb non-polar liquids only weakly if at all and adsorption of polar liquids is due to the orientation of the electric dipoles in their molecules in the electrostatic fields around the exchangeable ions held by the clay and around the negative charges on the clay substrate." Sideri (1937) believes that water adsorption and swelling of soil are determined by the structure of the surface layer of orientated particles.

On the basis of specific gravity, Perkins and King (1936) divided soil into separates and found that as the particle size decreased base exchange capacity increased per unit weight but decreased per unit surface area. Bray (1937) divided colloidal material (one micron and lower) into fractions 1.0 - 0.1 micron, 0.1 - 0.06 micron, and less than 0.06 micron in diameter. The base exchange capacity increased regularly with decrease in particle size. He attributed this, however, mainly to variation in minerals which make up the colloid and accompany the size variation rather than decreased particle size itself.



## EXPERIMENTAL PROCEDURE

### Division of the Soil into Fractions

The soil sample studied was taken from the B horizon of a Summit soil located on the campus of the Kansas State College of Agriculture and Applied Science. This is a residual soil with a relatively high percentage of colloidal material. One kilogram of soil was screened through a two mm. sieve to break down the lumps and separate out some of the roots. The sample was treated with hydrogen peroxide to remove the organic matter, using a modification of the method recommended by Olson and Bray (1938). Twenty gm. of soil and 160 ml. of 15 percent hydrogen peroxide were used in 800 ml. beakers instead of 5 gm. and 40 ml. in smaller beakers as recommended by these workers. Oxidation was allowed to proceed in covered beakers without heating until the reaction became slow. Then heat was applied by means of a steam bath until oxidation again subsided. Each operation required approximately two hours. Cover glasses were then removed and the sample evaporated to dryness. The organic-matter-free sample was put into a churn with five liters of distilled water and churned for a total of 140 hours. Within the first 100 hours of churning one part of ammonium hydroxide to 3000 parts of soil and water was



added at two different times as a dispersing agent, but this did not bring the colloidal material into suspension. The sample was also kneaded with the hands, and agitated in a small electric mixer for five minutes without satisfactory results. At this time small amounts were put into test tubes and varying quantities of .5 N sodium oxalate were added. The minimum amount of sodium oxalate which caused dispersion was one ml. to 25 ml. of soil and water. A proportionate amount was added to the original mixture and the soil churned for ten hours at which time dispersion appeared satisfactory. Ten minutes time was allowed for the sands to settle before the remaining suspended material was siphoned into another container. The sands were separated from the silt and clay in the sediment by means of washing over a 300 mesh screen. The sands were then fractionated by use of a nest of sieves. They fell mainly in the finer fractions so samples could not be obtained for fine gravel, coarse, medium, or fine sand.

The soil particles between 0.05 and 0.005 mm. in diameter were separated into four fractions, depending upon "effective" diameter, by gravity sedimentation using Stoke's law. Particles between 0.005 and 0.0005 mm. were separated into three fractions by use of an International Centrifuge No. 2. Sedimentation time was calculated in each case by

Stoke's law as applied to centrifuges by Svedberg and Nichols (1923). Particles below 0.0005 mm. were divided into four fractions by use of an International centrifuge No. 3.

The mathematical expression of Stoke's law as used for gravity sedimentation is:

$$t = \frac{h}{\frac{2}{9} g r^2 \frac{d_1 - d_2}{N}}, \text{ where,}$$

$h$  = height of column

$g$  = acceleration due to gravity

$r$  = radius of particle in cm.

$t$  = time in seconds

$d_1$  = density of soil particles (2.65)

$d_2$  = density of water (1.00)

$N$  = coefficient of viscosity of water at given temperature

A similar expression of Stoke's law as applied to centrifuges is:

$$t = \frac{h}{\frac{2}{9} r^2 \frac{d_1 - d_2}{N} \times 4 \pi^2 R a^2}, \text{ where}$$

$R$  = radius of centrifuge head

$a$  = speed in revolutions per second

Table 1 shows the calculated time of fall for the various sized particles and the means by which the separates were made, as well as the temperature involved. Centrifuge No. 3 builds up an inside temperature which is nearly constant at 35° C. This temperature was used for calculations on the two longest runs.

Table 1. Time of fall of particles and data used in its calculation.

Diameter in mm. lower limit	Settling force	Centrifuge speed r.p.m.	Distance of fall in cms.	Temperature degrees C.	T i m e	
					Hrs. Min.	Sec.
.050	Gravity		10	25		39.8
.035	"		10	25	1	21.2
.020	"		10	25	4	8.4
.010	"		10	25	16	34.8
.005	"		10	25	1 6	20.4
.0020	Centrifuge No. 2	480	12	25	9	54.0
.0010	"	1020	12	25	8	46.2
.0005	"	1200	12	25	25	20.4
.00020	Centrifuge No. 3	2200	13	25	44	9.0
.00009	"	2200	13	35	2 56	24.0
.00007	"	2200	13	35	4 51	24.0

The number of washings or redispersions necessary to eliminate particles smaller than the fractions themselves varied with the fractions. Each fraction was redispersed and resettled until the supernatant liquid showed only slight cloudiness. Table 2 shows the number of washings required for the various fractions.

Table 2. Calculated size of fractions and the number of washings required for purification.

Fraction No.	Size in mm.	Soil Separate	No. washings
1	0.1 - 0.05	Very fine sand	50
2	0.05 - 0.035	silt	50
3	0.035 - 0.020	"	30
4	0.020 - 0.010	"	35
5	0.010 - 0.005	"	35
6	0.005 - 0.002	"	30
7	0.002 - 0.001	clay	40
8	0.001 - 0.0005	"	30
9	0.0005 - 0.0002	"	20
10	0.0002 - 0.00009	"	20
11	0.00009 - 0.00007	"	15
12	below 0.00007		

Whitt and Baver (1937) in separating their fractions found many more washings necessary, however, their fractions were separated with a super-centrifuge. Joseph (1925) has indicated soil particles are not stable in the super-centrifuge and continue to break down. In the present study washing became difficult on fraction 9 so from this point

on the wash water was kept slightly alkaline by the use of sodium hydroxide.

Microscopic measurements were also made on the fractions large enough to be seen distinctly in an ordinary microscope. Two hundred twenty particles from each fraction were measured by means of an ocular scale. As expected, the fractions were not sharply defined within the size limits. Stoke's law measures only "effective" diameter, which varies with shape and density, while the microscope measures random diameters depending upon the way the particles rest upon the slide. A summary of the relationship of the microscopic measurements to particle size as determined by Stoke's law, is shown in Table 3.

Table 3. Summary of microscopic measurements.

Fraction Dia. mm.	68% between limits - mm.
0.10 - 0.05	0.078 - 0.041
0.05 - 0.035	0.054 - 0.033
0.035- 0.020	0.034 - 0.029
0.020- 0.010	0.020 - 0.011
0.010- 0.005	0.011 - 0.005
0.005- 0.002	0.006 - 0.002

### Hygroscopicity Determinations

Enough of each fraction to make 4 gm. of dry material was separated and put into individual centrifuge tubes for drying. Since sodium hydroxide had been used in the wash water it was also used in saturating the fractions with sodium ions. Two ml. of .1 N sodium hydroxide were added to the centrifuge tubes, stirred, and the particles settled by gravity or by centrifugal force depending upon their size. This treatment was repeated to insure saturation of the fractions. An attempt was made to remove the excess ions by washing with distilled water before washing with alcohol. A special drying process was necessary to keep the fractions in satisfactory physical condition for future determinations. Ninety-five percent ethyl alcohol was applied and poured off twice, absolute ethyl alcohol once, and anhydrous ether once. Air, dried by calcium chloride, was drawn over the ether-treated samples by a vacuum pump. Fraction 12 was too fine to be thrown out of suspension by centrifugal force so a representative portion was collected on a Pasteur-Chamberland filter and immersed into cylinders containing the following solutions: sodium hydroxide, distilled water, 95 percent ethyl alcohol, absolute alcohol, and anhydrous ether, in the order named. The solutions were

forced through the colloid and filter by application of suction from a vacuum pump. This process required approximately three hours for each solution. The fraction was then transferred to a centrifuge tube and dried in the same manner as the others. Duplicate samples containing approximately 2 gm. of each of the first five fractions and 1 gm. of each of the remaining fractions were weighed into dry weighing bottles, 25 by 50 mm. in size. The amount of sample was cut from 2 gm. to 1 gm. in order to keep the depth of the sample in the weighing bottle nearer a constant. The bottles with lids removed were placed in a humidifier over 30 percent sulfuric acid at 25° C. and left for five days. The humidifier was evacuated to a pressure of approximately 16 cm. of mercury. At the end of the period dry air was slowly let into the humidifier to prevent condensation of moisture inside. When pressure equilibrium was attained the humidifier lid was removed and weighing bottle lids placed into position as soon as possible. The bottles were then placed into a desiccator and taken outside the constant temperature room to come to equilibrium before weighing. Several empty weighing bottles were carried along to determine the amount of moisture taken up by the bottle. The percentage moisture adsorbed by the soil fractions was inconsistent when figured on the ether dry basis



so the bottles containing the separates were put into the oven. Heat was applied at  $95^{\circ}$  C. for 43 hours and at  $105^{\circ}$  C. for 66 hours before the loss in weight of the finer fractions became low enough to be considered within experimental error. Hygroscopicity over 30 percent sulfuric acid was again determined in the same manner as before. At the end of this period hygroscopicity over 3.3 percent sulfuric acid was determined under the same conditions as over the 30 percent acid. Hygroscopicity for calcium and potassium treated fractions was determined in the same manner as for the sodium separates except hygroscopicity was not determined before oven drying which required 75 hours at  $105^{\circ}$  C. in both cases. The samples were saturated with calcium and potassium by the use of .1 M  $\text{Ca}(\text{NO}_3)_2$  and .1 M  $\text{KNO}_3$ , respectively. Fraction 7 was omitted from the potassium determination because of lack of material. It was assumed oven drying at  $105^{\circ}$  C. had little effect upon hygroscopicity of the separates. Bouyoucos (1925) found that the heat of wetting of colloids was not affected by heating below  $200^{\circ}$  C. Bayer and Horner (1935) observed that water adsorption was almost reversible as long as the colloid was heated at temperatures below the "minimum point." The lowest minimum point found by them was  $125^{\circ}$  for the Cecil colloid.

## EXPERIMENTAL RESULTS AND DISCUSSION

A summary of the average percentages of water adsorbed by duplicate samples from the atmosphere over 30 percent and 3.3 percent sulfuric acid is given in Table 4. The data show that in general the amount of water adsorbed at each degree of humidity increased as the size of the particles decreased. However, the surface area increased more rapidly than the percentage of water adsorbed.

Fraction 2 adsorbed less water than fraction 1 in all six cases examined, thus making a break in the curves as shown by Figs. 1 and 3. The direction of the curve for particles larger than those of fraction 1 cannot be determined for the soil used due to the absence of particles greater than .1 mm. in diameter. The almost straight line relationship between the surface area and percentage of water adsorbed by fractions 2 to 7, inclusive, indicates a close correlation between adsorption and surface area. This does not hold for fractions 8 to 12, inclusive, and a distinct break occurs in the region of fraction 7. The exact cause of this break is undetermined but it is possibly due to a change in the mineral nature of the soil particles. Marshall, as quoted by Russell (1937) p. 171, found that the percentage of quartz in soil fractions became greatly

Table 4. Adsorption of water by the fractions saturated with different cations.

Fraction number	Surface area $\text{cm}^2/\text{gm}$	Percentage $\text{H}_2\text{O}$ adsorbed from atmosphere above indicated concentrations of sulfuric acid.									
		Na		Ca		K					
		50%	30%	5.3%	30%	5.3%	30%	5.3%	30%	5.3%	30%
1	301	.142	.230	.493	.248	.493	.208	.478			
2	533	.094	.082	.355	.167	.366	.163	.443			
3	823	.161	.163	.641	.260	.753	.216	.654			
4	1,509	.265	.294	1.002	.417	1.208	.366	1.034			
5	3,019	.565	.615	1.753	.803	2.234	.651	1.720			
6	6,469	.870	.890	2.937	1.315	3.555					
7	15,094	1.392	1.470	3.876	1.529	4.195	1.255	3.382			
8	30,189	3.800	---	12.696	5.006	12.670	4.371	11.591			
9	64,690	6.422	6.867	20.170	6.572	19.629	5.826	18.828			
10	156,148	9.264	10.125	30.145	10.441	35.393	9.512	35.099			
11	283,019	11.706	12.708	40.036	13.240	40.191	12.152	38.832			
12	637,789	17.410	18.501	44.159	18.272	45.471	13.416	35.877			

\* This determination was made on ether dried fractions before being oven dried.

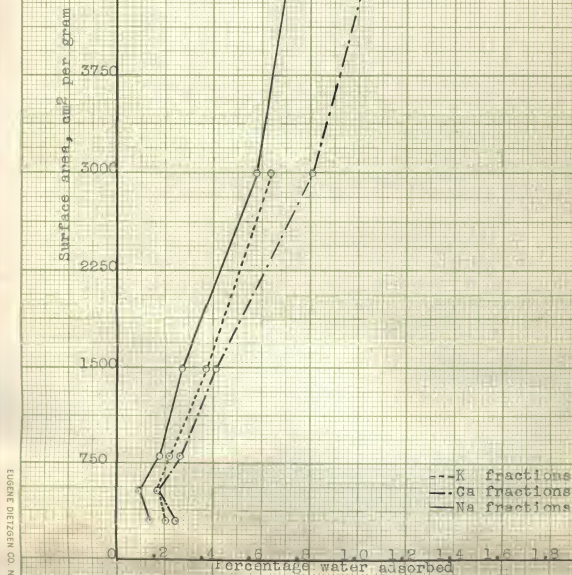


Fig. 1. Surface area vs percentage moisture adsorbed over 30 percent sulfuric acid for fractions 1 to 6 inclusive.

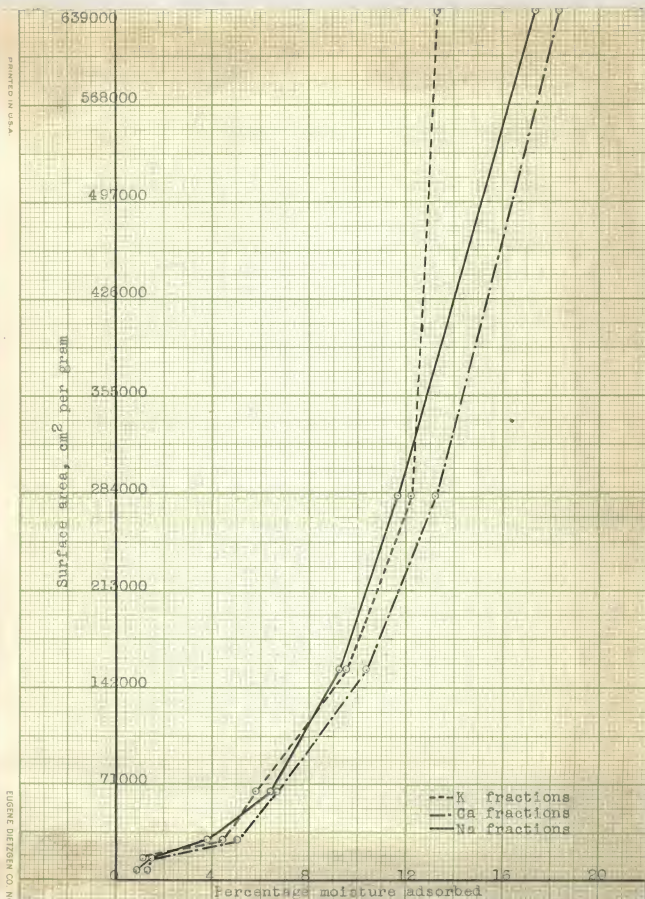


Fig. 2. Surface area vs percentage moisture adsorbed over 30 percent sulfuric acid for fractions 6 to 12 inclusive.



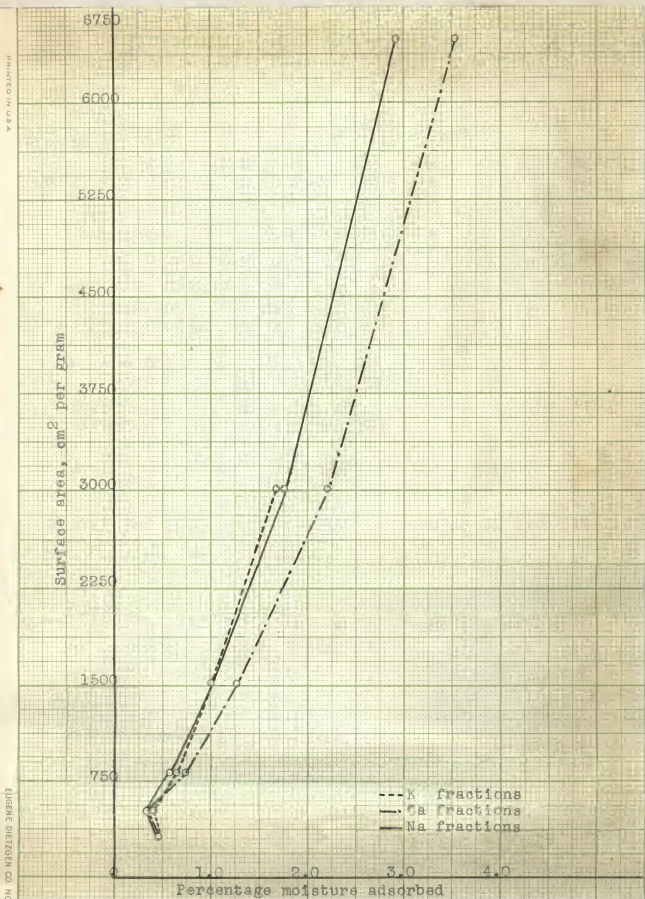


Fig. 3. Surface area vs percentage moisture adsorbed over 3.3 percent sulfuric acid for fractions 1 to 6 inclusive.

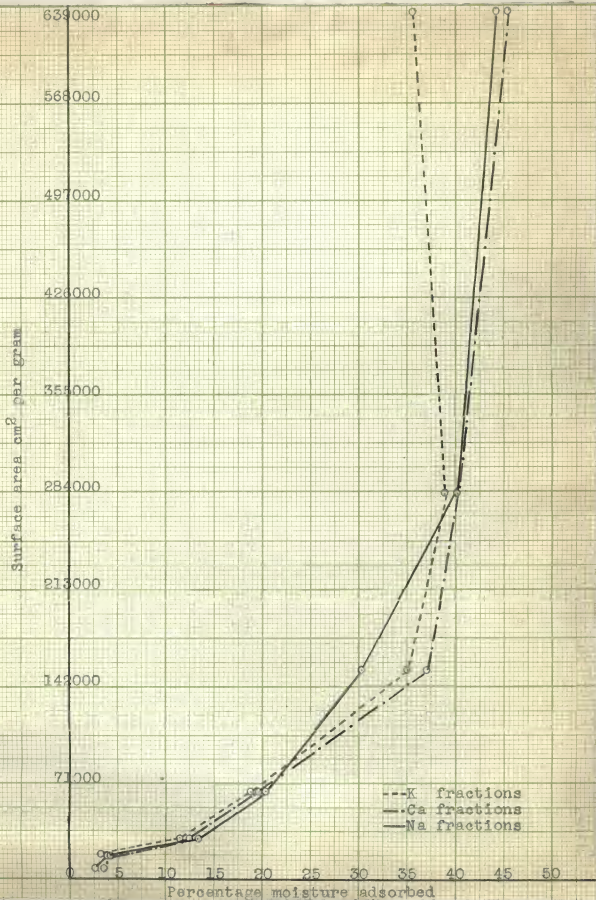


Fig. 4. Surface area vs percentage moisture adsorbed over 3.3 percent sulfuric acid for fractions 6 to 12 inclusive.



reduced in approximately the same region and that clay minerals increased. Whitt and Baver (1937) also indicated a probable change in mineral composition in this region exhibited by a wide break in base exchange capacity and absence of swelling in particles greater than .001 mm. in diameter.

Table 5 gives the adsorption per ten thousand square cm. of surface area as calculated from the percentage figures presented in Table 4. This table shows quite distinctly that adsorption of water per unit area of surface decreases as the particle size decreases. The greatest reduction in adsorptive power per unit area of surface occurs between fractions 1 and 2. The remainder of the curve is quite irregular but has a distinct downward trend. The break in this downward trend in the region of fraction 7 was previously discussed.

Adsorption as affected by the cations used was somewhat irregular. Considering the results from exposure to the atmosphere over 30 percent sulfuric acid the calcium treated fractions were high in all cases, and sodium treated ones were low in all except three cases. Exposure to the atmosphere above 3.3 percent sulfuric acid resulted in calcium treated samples having greatest adsorption in all except three cases, and potassium the least in all except four cases. The order of  $\text{Ca} > \text{K} > \text{Na}$  for adsorption from the

Table 5. Water adsorption per ten thousand square cm. of surface area.

Fraction number	Factor	Percentage H <sub>2</sub> O adsorbed per 10,000 cm <sup>2</sup>					
		Na		Ca		K	
		Over 30%	Over 3.3%	Over 30%	Over 3.3%	Over 30%	Over 3.3%
1	33.222	4.718	16.378	8.239	16.378	6.910	15.880
2	18.762	1.764	6.661	3.133	6.867	3.058	8.312
3	12.151	1.956	7.789	3.159	9.150	2.625	7.947
4	6.627	1.743	6.640	2.763	8.668	2.425	6.852
5	3.312	1.871	5.806	2.660	7.399	2.090	5.696
6	1.546	1.345	4.541	2.033	5.496		
7	.663	.923	2.570	1.014	2.781	.832	2.242
8	.331	1.258	4.202	1.657	4.194	1.447	3.770
9	.156	1.002	3.147	1.025	3.062	.909	2.937
10	.064	.593	1.929	.668	2.265	.609	2.246
11	.0353	.413	1.413	.467	1.419	.429	1.371
12	.0157	.273	.693	.287	.714	.211	.563

atmosphere over 30 percent sulfuric acid agrees with the results of Anderson (1929).

More moisture was adsorbed from the atmosphere of the higher relative humidity than from that of the lower relative humidity but with no constant relationship. Oven drying lowered the percentage of water adsorbed from that of the ether dry samples in all cases. The amount of lowering was small enough to justify oven drying.

#### SUMMARY

A sample from the B horizon of a Summit soil from the campus of Kansas State College of Agriculture and Applied

Percentage moisture adsorbed over 30% sulfuric acid per 10,000 cm<sup>2</sup> surface area

---K fractions  
 ---Ca fractions  
 ---Na fractions

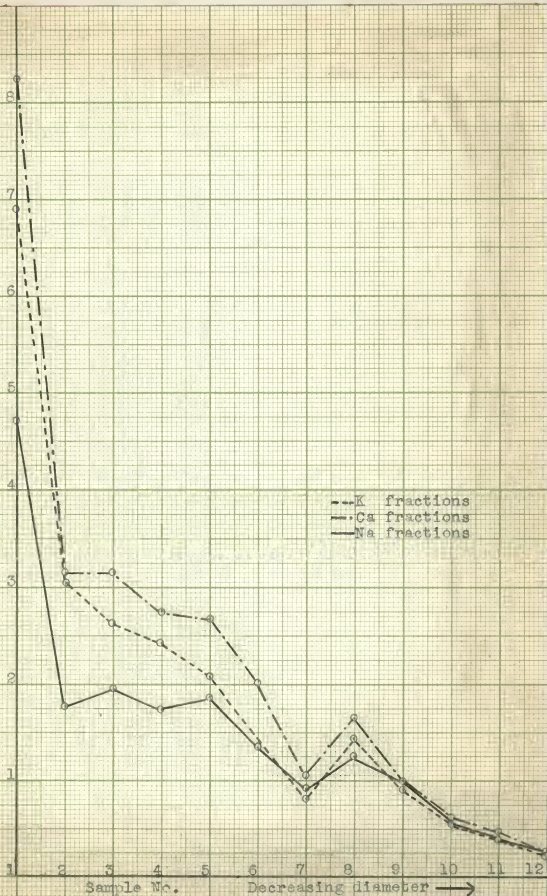


Fig. 6. Sample No. vs percentage moisture adsorbed over 30 percent sulfuric acid per 10,000 cm<sup>2</sup> surface.

Percentage moisture adsorbed over 3.3% sulfuric acid per 10,000 cm<sup>2</sup> surface area

---K fractions  
---Ca fractions  
—Na fractions

Sample No.      Decreasing diameter →

Fig. 6. Sample No. vs percentage moisture adsorbed over 3.3 percent sulfuric acid per 10,000 cm<sup>2</sup> surface.

Science was divided into 12 fractions below .10 mm. according to "effective" diameter. The amount of water adsorbed from the atmosphere over 30 percent and 3.3 percent sulfuric acid was determined for the fractions saturated with Na, Ca, and K cations.

As the size of particle decreased the amount of water adsorbed per unit weight increased. The increase in adsorption was not proportional to the increase in surface area when exposed to either of the two atmospheres. The amount of water adsorbed per unit area of surface decreased as the size of particle decreased, but not as a straight line function.

At the lower relative humidity adsorption by the fractions treated with the various cations ranked in the following order,  $\text{Ca} > \text{K} > \text{Na}$ . For the higher relative humidity the ranking was  $\text{Ca} > \text{Na} > \text{K}$ , with only small differences.

Adsorption over 3.3 percent sulfuric acid was greater than that over 30 percent acid but with no constant relationship. Oven drying of the fractions at  $110^{\circ}\text{C}$ . only slightly lowered the hygroscopicity.

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